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CONTTROLLED GROWTH OF IRON OXIDE MAGNETIC NANOPARTICLES VIA CO-PRECIPITATION METHOD AND $NaNO_3$ ADDITION

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ABSTRACT

CONTROLLED GROWTH OF IRON OXIDE MAGNETIC NANOPARTICLES VIA COPRECIPITATION METHOD AND $NaNO_3$ ADDITION. Size controlled magnetic nanoparticle (MNPs) of iron oxide were prepared in the presence of $NaNO_3$ via co-precipitation method followed by HNO_3 peptizing according to Massart's method. The MNPs size were reduced by addition of $NaNO_3$ in varied molarity and at different stage of process. As an end product, stable water-base colloids were formed. XRD pattern analysis using Rietveld method confirmed Fe_3O_4/γ-Fe_2O_3 phase formation with nanoscale crystallite size. This crystallite size significantly decrease with $NaNO_3$ addition from 12 nm to smaller than 8 nm, and give end-result of decreasing magnetization as measured by VSM. Langevin fitting of magnetic hysteresis curve also revealed the magnetic core size of nearly the same behaviour. TEM results show bigger value for single magnetic nanoparticle of > 10 nm and < 10 nm for MNPs without and with $NaNO_3$ addition, respectively. However, PSA measurement still trace a low nanoparticle agglomeration of ~ 20 nm, even after surface peptization using HNO_3. A possible mechanism is proposed to explain these characteristics formation especially of the MNP's size.

Keywords: Magnetic nanoparticle, Fe_3O_4, γ-Fe_2O_3, $NaNO_3$, Size

ABSTRAK

PENGENDALIAN PENUMBUHAN NANOPARTIKEL MAGNETIK OKSIDA BESI DENGAN METODA KO-PRESIPITASI DAN PENAMBAHAN $NaNO_3$. Nanopartikel magnetik oksida besi dengan ukuran terkendali telah dipreparasi dengan metoda ko-presipitasi dan penambahan $NaNO_3$ serta peptisasi HNO_3 mengikuti metoda Massart. Pengendalian ukuran nanopartikel magnetik dilakukan dengan memvariasikan nilai molaritas serta tahapan proses penambahan $NaNO_3$. Hasil analisis pola difraksi sinar-X dengan metoda Rietveld mengkonfirmasi terbentuknya fasa Fe_3O_4/γ-Fe_2O_3 dengan penurunan ukuran kristalit dari 12 nm untuk sampel tanpa penambahan $NaNO_3$ menjadi 8 nm setelah penambahan $NaNO_3$. Pengecilan ukuran ini juga teranalisis pada hasil *fitting* kurva magnetisasi dengan persamaan Langevin serta pengamatan dengan TEM. Namun hasil pengukuran PSA tetap mendeteksi adanya aglomerasi nanopartikel dengan ukuran aglomerat terkecil ~20 nm meski telah dilakukan upaya peptisasi dengan HNO_3. Mengacu pada berbagai data karakteristik dan hasil analisis ini, mekanisme pengendalian pertumbuhan ukuran partikel ini dicoba dijelaskan dalam artikel ini.

Kata kunci: Nanopartikel magnetik, Fe_3O_4, γ-Fe_2O_3, $NaNO_3$, Ukuran

INTRODUCTION

Synthesis of iron oxide magnetic nanoparticles with small and uniform size is still a challenge for researchers to date, mainly motivated by the growing extent of the potential application of these nanoparticles [1]. Each application has a specific requirement for a magnetic nanoparticle to be used, either size, surface properties or its other physico-chemical properties [2].

Iron oxide nanoparticles can be synthesized by various methods including co-precipitation, microemulsion, thermal decomposition, and mechanical synthesis [3]. The co-precipitation method is more common method compare to the others due to its simple, save and economic procedure. The process of co-precipitation involves initial nucleation followed by slow growth as the solutes diffuse to the surface of the crystal. The size and other properties of the growth nanoparticles will be altered by some parameters including pH, temperature, reaction time, and iron ion ratios [4]. Normal co-precipitation method usually produce nanoparticles in the size range of 10 to 40 nm and the maximum magnetic saturation could reach almost 90 emu/gram. However, some application prerequest the nanoparticles with smaller size while maintaining its high magnetic saturation value, in the form of water-base stable colloid.

Stable colloid usually synthesizes following the Massart's method in which nanoparticle surface are peptisized by acidic or alkaline surfactant such as HNO_3, $HClO_3$ and TMAOH [5]. In some research, for reducing nanoparticles size, counter ion was added to increase its ionic strength within precipitation process. Some type of counter ion usually used are $NaNO_3$,NH_4NO_3 or $N(CH_3)_4NO_3$ which result in nanoparticle size smaller than 10 nm, even on the size as small as ~ 2nm [6]. But there is no clear explanation about its magnetic value and the mechanism of size reduction.

In this article, the mechanism of this size controlled was discussed and a model was proposed to get more complete understanding about the role of $NaNO_3$ counter ion on the size reduction of magnetic nanoparticle. The data was collected from serial magnetic nanoparticles synthesized by addition of $NaNO_3$ in varied molarity and at different stage of coprecipitation process, followed by peptisizing with HNO_3.

EXPERIMENTAL METHOD

Materials

The chemical used in the synthesis of magnetic nanoparticles are $FeCl_2.4H_2O$, $FeCl_3.6H_2O$, NaOH, $NaNO_3$, HNO_3 from Merck, Germany with pro analysis grade (pa) and deionized water of 18.2 MΩcm^{-1}.

Synthesis of Magnetic Nanoparticles

Magnetic nanoparticles were synthesized by co-precipitation method. Fe (II) and Fe (III) salt in a mole ratio of 1: 1 were dissolved in deionized water. Mixed solution of Fe-salt was added at once into NaOH solution of 3.2 M to nucleate the precipitation, continued with ultrasonic mixing for 5 minutes to ensure formation of nanoscale iron-oxide particles. For original sample, the process was continued with aging the solution overnight for enhancing crystallization process of iron oxide phase. Magnetic precipitates were separated from its supernatant by using permanent magnet. Peptizing of nanoparticles were done following the Massart's method by adding HNO_3 to get acidic sol [5]. The process was done ultrasonically for 2 minutes, followed by decantation of supernatant by centrifugation at 9000 rpm for 10 minutes. To get end result of stable water-base magnetic colloid, the precipitates were dissolved in deionized water and ultrasonically stirred for 5 minutes. 2 mL of samples were evaporated to get dry powder sample for characterization.

Modified samples with $NaNO_3$ were done in varied manner as listed in Table 1. Two different stages of $NaNO_3$ addition were choosen, either mixed together with Fe(II)/Fe(III) salt before precipitation or added after precipitation of Fe(II)/Fe(III) with NaOH.

Table 1. List of the prepared magnetic nanoparticles

No.	Sample Code	Magnetic nanoparticle modification
	1st-series, peptizing with varied HNO_3 molarity, without $NaNO_3$ addition	
1.	Na0H0	M (HNO_3) = 0
2.	Na0H0.2	M (HNO_3) = 0.2
3.	Na0H0.4	M (HNO_3) = 0.4
4.	Na0H0.6	M (HNO_3) = 0.6
	2nd-series, fix HNO_3 molarity of 1M and varied molarity of $NaNO_3$ added before precipitation process	
1.	Na2H1B	M ($NaNO_3$) = 2M
2.	Na4H1B	M ($NaNO_3$) = 4M
3.	Na6H1B	M ($NaNO_3$) = 6M
4.	Na8H1B	M ($NaNO_3$) = 8M
5.	Na10H1B	M ($NaNO_3$) = 10M
	3rd-series, fix HNO_3 molarity of 1M and varied molarity of $NaNO_3$ added after precipitation process	
1.	Na2H1A	M ($NaNO_3$) = 2M
2.	Na4H1A	M ($NaNO_3$) = 4M
3.	Na6H1A	M ($NaNO_3$) = 6M
4.	Na8H1A	M ($NaNO_3$) = 8M
5.	Na10H1A	M ($NaNO_3$) = 10M
	4th-series, fix $NaNO_3$ of 6M molarity added before precipitation and varied HNO_3 molarity	
1.	Na6H0	M (HNO_3) = 0
2.	Na6H0.2	M (HNO_3) = 0.2
3.	Na6H0.4	M (HNO_3) = 0.4
4.	Na6H0.6	M (HNO_3) = 0.6

Characterization of Magnetic Nanoparticles

Dry powder was characterized by X-ray diffractometer (XRD) with Cu-Kα targets to identify the phases and nanoparticles crystallites size. Data were collected with XRD PANAnalytical model Empyrean at diffraction angle of 20^o to 80^o. Phases were identified using Rietveld analysis method implemented in RIETAN-2000 software package [7] using 2-phases assumption of Fe_3O_4 (JCPDS No.82-1533, *space group Fd3m*) and α-Fe_2O_3 (JCPDS No. 39-1346, *space group P4$_1$32*), while crystallite size of the nanoparticles were calculated using Debye-Scherrer equation. Morphology of static size of magnetic nanoparticles was observed using Transmission Electron Microscope (TEM) JEOL JEM 1400 for colloid samples diluted 5 folds before measurement. The size distribution of NPs in colloidal system were analyzed using Particle Size Analyzer Malvern NanoZetasizer also using 5-fold diluted samples. Magnetic hysteresis curve was measured using a Vibrating Sample Magnetometer (VSM) of OXFORD 1.2H with a measurement speed of 0.25T / min. The hysteresis curves were further fitted using Langevin function of superparamagnetic system for determining magnetic size of nanoparticles.

RESULT AND DISCUSSION

XRD Pattern Analysis

Generally, all samples displayed typical Fe_3O_4/γ-Fe_2O_3 XRD pattern as shown in Figure 1, ensuring no other oxide and non-magnetic phase formation. The difference between original and after modified samples are only noticed in its peak broadening behaviour showing different degree of crystallinity of each sample. Figure 2 shows some of Rietveld refinement result using RIETAN2000 program for sample before and after modification. From this refinement, informations including type of phases, their % weight fraction and FWHM (full width half maximum) data could be obtained. This FWHM value contains information about crystallinity of the samples in which bigger FWHM value, more broader peaks and more amorphous the samples. Crystallite size of the sample could be calculated by Debye-Scherrer equation of:

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad \text{..............................} \ (1)$$

k = A constant related to instrumental arrangement has a value of 0.916

λ = Wavelength of Cu-K_α X-ray source equal to 1.5406 Å

β = Denoted for FWHM

θ = Diffraction angle of the peak respectively

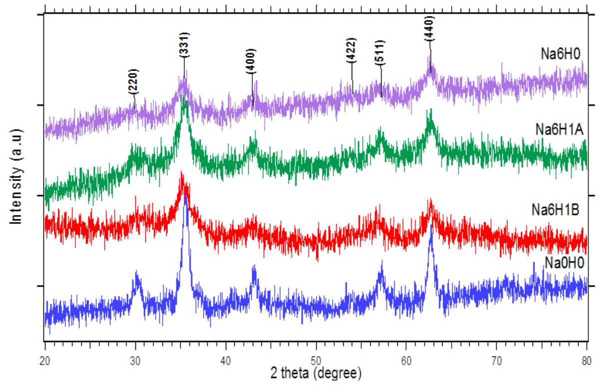


Figure 1. X-ray diffraction pattern of (from the bottom to the top): Na0H0, Na6H1B, Na6H1A, Na6H0 samples

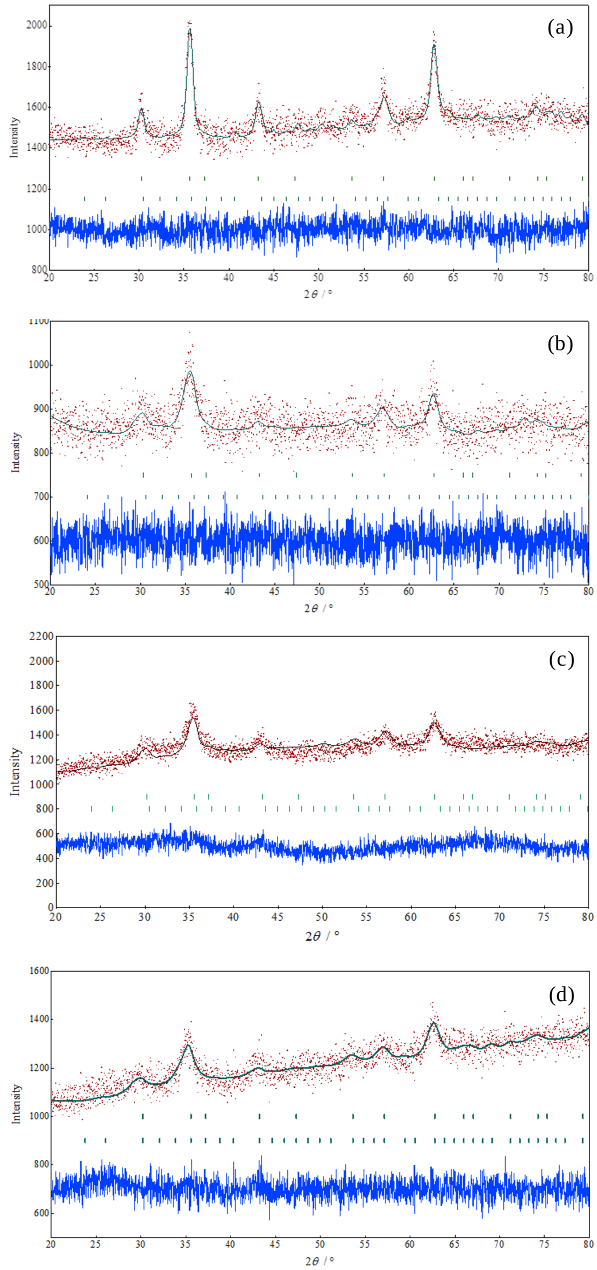


Figure 2. Rietan profile for Na0H0, Na6H1B, Na6H1A and Na6H0 samples (from top to the bottom).

Table 2. Characteristic of Magnetic Nanoparticles Fe_3O_4/γ-Fe_2O_3 after some modification with $NaNO_3$ and HNO_3

No.	Sample Code	Phase fraction of Fe_3O_4 (%)	Ms (emu/gram)	Particle Size (nm)			
				PSA	TEM	XRD	VSM
			1st-series				
1.	Na0H0	0.2445	77.97	268.08	> 10	11.53683	8.43555
2.	Na0H0.2	0.2693	65.58	127.58		12.73387	9.09387
3.	Na0H0.4	0.6154	49.61	84.78		13.07568	10.2102
4.	Na0H0.6	0.566	46.33	85.58		10.86988	10.282
			2nd-series				
1.	Na2H1B	0.6909	41.89	62.94		6.391233	8.80253
2.	Na4H1B	0.5711	38.04	46.04		5.064378	8.90071
3.	Na6H1B	0.4751	37.25	31.60		6.767192	8.4052
4.	Na8H1B	0.4990	40.76	118.3		5.701094	8.0476
5.	Na10H1B	0.4136	32.00	49.38		4.902013	8.54175
			3rd-series				
1.	Na2H1A	0.5004	41.44	60.85		6.185035	8.84123
2.	Na4H1A	0.3906	36.97	71.08		3.864834	9.09461
3.	Na6H1A	0.4355	43.97	20.02		8.225166	8.91152
4.	Na8H1A	0.4639	36.49	181.20		4.487137	8.94456
5.	Na10H1A	0.4865	35.10	109.10		7.372910	8.56649
			4th-series				
1.	Na6H0	0.5172	38.50	65.10	< 10	5.129831	8.38461
2.	Na6H0.2	0.4378	41.02	25.75		7.160345	8.87663
3.	Na6H0.4	0.5415	30.36	27.30		7.811543	9.35783
4.	Na6H0.6	0.4679	34.01	27.10		7.732329	8.953

Complete phase identification and crystallite size calculation result of all the samples are presented at Table 2.

Data on Table 2 show that HNO_3 peptizing have the role on controlling the growth of Fe_3O_4 phase in which higher HNO_3 molarity will result in higher Fe_3O_4 weight fraction. The crystallite size tends to be un-affected by HNO_3 modification. $NaNO_3$ addition give more pronounce effect on nanoparticle crystallite size. The stage of $NaNO_3$ addition is also affecting the growth of magnetic nanoparticle crystalline. The crystallite size of the 2nd series are more stable related to $NaNO_3$ molarity changing compared to the 3rd series samples. However, crystallite sizes of the 3rd series samples are only randomly related to the $NaNO_3$ molarity and magnetic nanoparticle of as low as 3 to 4 nm crystallite size could be achieved.

TEM Observation

Figure 3 displayed the TEM photograph of typical morphology of magnetic nanoparticle without and after having some modification with HNO_3 and $NaNO_3$. Generally, the photograph clearly displayed spherical nanoparticle with different pattern of agglomeration. For samples without modification, Na0H0 at Figure 3(a), magnetic nanoparticle tend to agglomerate with the size of more than 10 nm.

Peptizing with HNO_3 made the magnetic nanoparticle are more separated to each other, leaving only a slight agglomeration, but with the nanoparticle size of still around 10 nm. Nanoparticle size of $NaNO_3$ modified samples are more uniform in the range smaller than 10 nm but with no significant difference between 2nd series and 3rd series samples. It could be assumed that HNO_3 have a role on dispersing the magnetic nanoparticle within the medium and will be responsible for stabilizing the magnetic nanoparticle colloid. These TEM data were also picturing the role of $NaNO_3$ on reducing magnetic nanoparticles size, which fit with magnetic nanoparticle crystallite size behaviour analyzed from XRD pattern.

PSA Data

Agglomeration tendency of any colloidal samples could be analyzed using dynamic laser scattering (DLS) technique. This technique usually implemented on Particle Size Analyzer (PSA) instrument which measures the "real" particle size within the colloid samples and usually describe as distribution curve of groups of magnetic nanoparticle with specified size range. Such distribution curve of magnetic nanoparticle synthesis in this experiment are shown in Figure 4.

The curve show the maximum particle distribution at the size of more than 260 nm for the sample without any modification (Figure 4(a)) and at the size of around 20 nm for after $NaNO_3$ modification. Complete data of particle size measured by PSA are listed at Table 2.

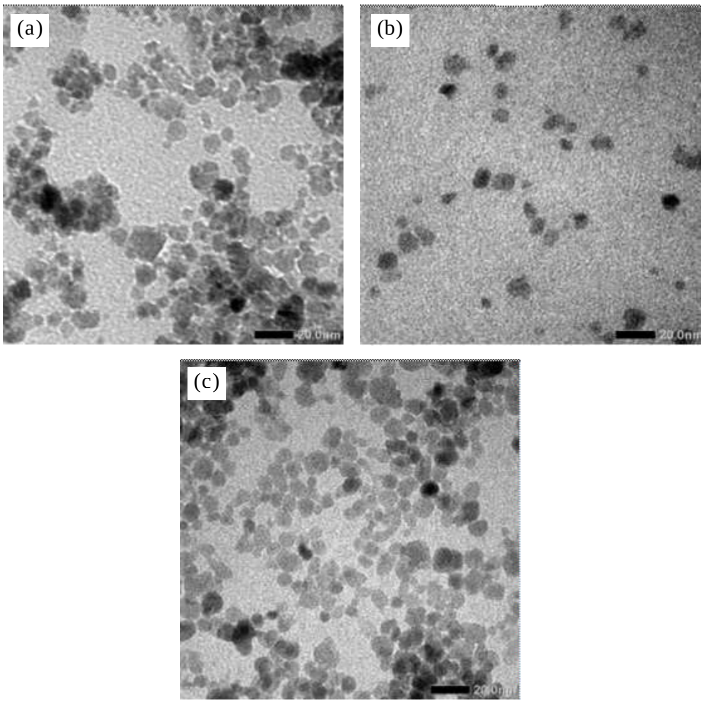


Figure 3. TEM photograph of (a). Na0H0, (b). Na0H1 and (c). Na6H1B samples (the scale bar is equal to20 nm).

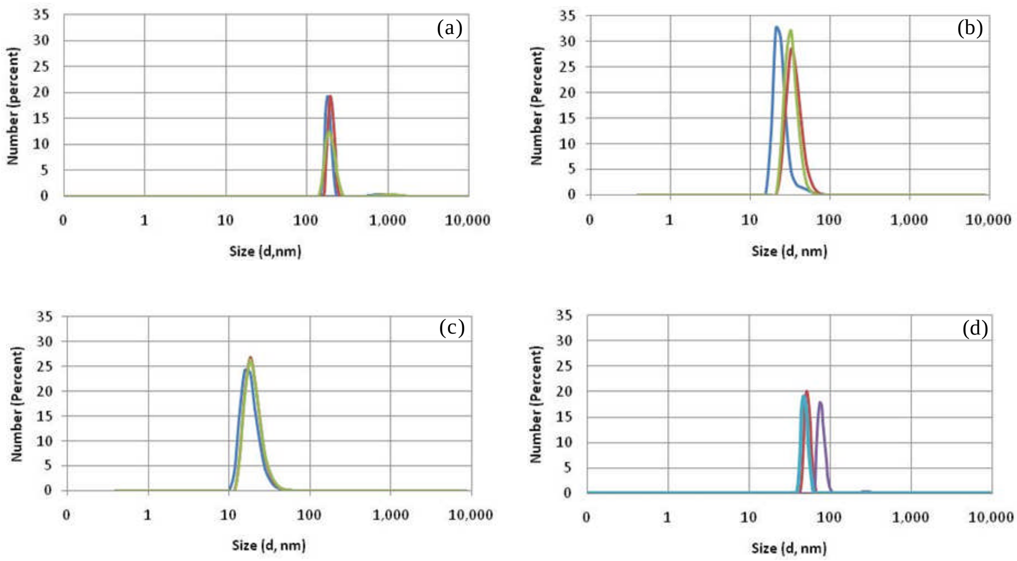


Figure 4. Size distribution curve of (a). Na0H0; (b). Na6H1B; (c). Na6H1A and (d). Na6H0 samples.

Referring to the single particle size measured by TEM, these PSA data could be considered as the size of a group of particles which forming agglomeration within the colloid. A significant decrease of the size with increasing HNO_3 molarity for 1st series samples indicates that HNO_3 will modify nanoparticles surface and inhibited agglomeration possibility between the particles. At the contrary, $NaNO_3$ modification will give contra-productive result on nanoparticle agglomeration tendency. There is an optimum $NaNO_3$ molarity that give smallest agglomerate in the size of around 20 nm for samples modify with 6M $NaNO_3$. PSA data of the 4th-samples revealed the same size which affected no more with increasing of HNO_3 molarity. For higher HNO_3 molarity, the agglomerates tend to increase again to hundreds size.

Magnetic Hysteresis Curve Analysis

Magnetic properties of nanoparticles system usually analysed from its magnetic hysteresis curve. The curve is generated by measuring the magnetic flux or magnetization (M) of a ferromagnetic material while the magnetizing force (H) is changed. Figure 5

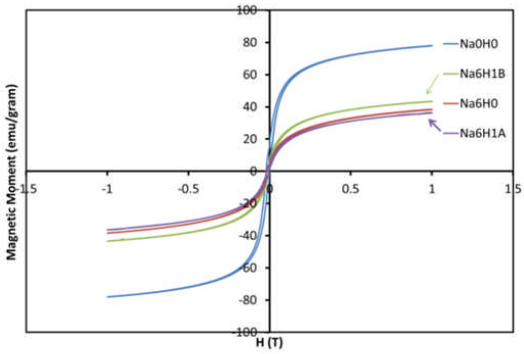


Figure 5. Magnetic hysteresis curve of Na0H0, Na6H1B, Na6H1A and Na6H0 samples.

showed the curve for some samples with different synthesis parameters, which show typical curve for superparamagnetic materials. For sample without any modification, Na0H0, magnetization was saturated at M_s value of 78.14 emu/gram and decreased to a range of 30 to 40 emu/gram after HNO_3 and $NaNO_3$ modification with HNO_3 modification being more responsible than $NaNO_3$.

For superparamagnetic systems, magnetization values as a function of the external field, M (H) at T> T_B could be modeled using Langevin function approach, L (α) and Equation [8]:

$$M(H) = M_s L(\alpha) \quad \text{.............................} \quad (2)$$

In which M_s is spontaneous magnetization, k_B is Boltzmann constant equal to 1.38064852 x 10^{-23} J/K, m is magnetic moment for 1 particle unit

$$L(\alpha) = \coth\alpha - \frac{1}{\alpha} \quad \text{....................} \quad (3)$$

$$\alpha = \frac{mH}{k_B T} = aH \quad \text{..............................} \quad (4)$$

For spherical magnetic nanoparticle,

$$m = M_s w = M_s \rho V = \frac{\pi}{6} d^3 M_s \rho \quad \text{.........} \quad (5)$$

with ρ being density of mass of Fe_3O_4. From Equation (4) and Equation (5),

$$d = \sqrt[3]{\frac{6k_BT}{\pi\rho}\left[\frac{a}{M_s}\right]} \quad \text{................................} \quad (6)$$

Typical fitting result of the samples are presented at Figure 6. Form this fitting, it was found that the d-value of magnetic cores for samples without $NaNO_3$ modifications were around 10 nm, while for $NaNO_3$-modified samples were 8 to 9 nm. Complete magnetic core value of all the sample are listed at Table 2.

Controlled Growth Mechanism of Magnetic Nanoparticles

Data on Table 2 shows some characteristic behaviour of magnetic nanoparticles related to the

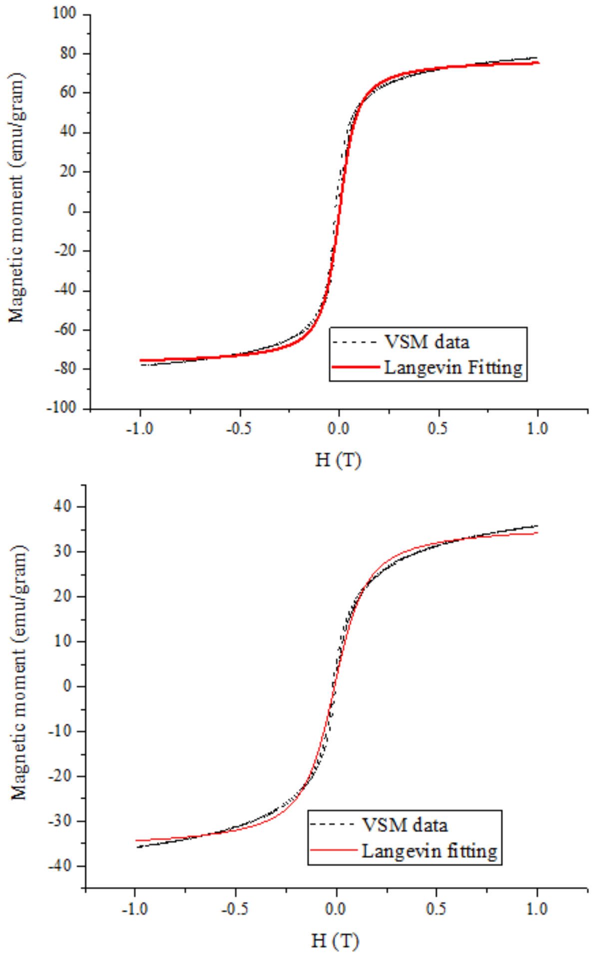
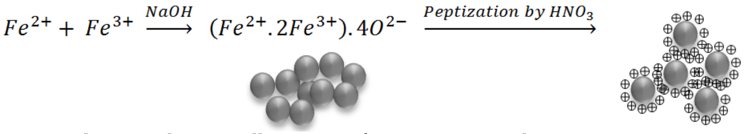


Figure 6. Langevin Fitting of Na0H0 and Na6H1B samples.

modification with HNO_3 and $NaNO_3$. It can be resumed that three characteristics including magnetization, crystallization and particle size were all depend on some sort to the modification. HNO_3 modification shows more pronounce effect on magnetization and agglomeration, while addition of $NaNO_3$ affected more on magnetic nanoparticle crystallinity which also depend on the stage of $NaNO_3$ addition.

Principally, co-precipitation process on magnetic nanoparticles synthesis usually involves several steps including nucleation of precipitate, growth of precipitate and completion of magnetic nanoparticles phases [4]. At nucleation stage, Fe^{2+} and Fe^{3+} ions will react with O^{2-} from NaOH base immediately after mixing which represent as the direct change of solution colour from yellowish to black solution and forming magnetic nanoparticles nuclei. These nuclei then growth with more diffusion of the ions afterward to the nuclei and arrange them to build crystal structure and phases favour for the system, which take time during overnight aging. At the end of the reaction, system will have a high alkaline environment at high pH ~ 12 and chlorine residue within medium.



Gambar 7. Schematic illustration of precipitation and peptization on iron oxide magnetic nanoparticles.

Without further peptization, the precipitate, earned after several washing steps until neutral pH, will be agglomerated due to strong magnetic interaction between nanoparticles and will result in un-stable magnetic liquid. Massart's method solve this problem by peptization of nanoparticles surfaces with acidic or alkaline surfactant such as $HClO_3$ and TMAOH respectively [5]. The magnetic sol formed after peptization will be easily dispersed in water and give stable colloid system. Such processing step is schematically present at Figure 7.

From this schema, it could be figure out the function of HNO_3 on stabilizing magnetic nanoparticle within water medium. magnetic nanoparticle will be separated by positive polar repulsion and bound to medium via hydroxyl group [9]. As a result, the magnetic nanoparticle will be attracted by magnet as a magnetic liquid, instead of as separate magnetic particle which can be seen in Figure 8.

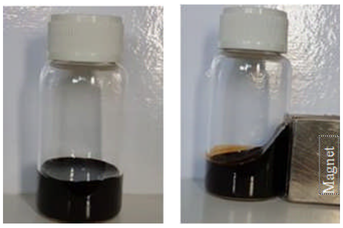


Figure 8. Photo of liquid magnetic sample before (left) and after (right) attracted by permanent magnet.

For samples with low molarity of HNO_3, the magnetic interaction between the nanoparticles remained strong and led to the agglomeration. Increasing HNO_3 molarity, will give thicker layer of surfactant. As the results, the particles are more separated, agglomerate size will be decreased and more stable colloid will be obtained. However magnetic interaction between nanoparticles will also be weakened and there is a dilution effect to the magnetic fraction which consequently decreasing the magnetization value. The size of crystalline show no significant relation to HNO_3 addition, which confirm that the growth of nanoparticle size are already completed within overnight-aging time or before peptization [10].

On the other hand, addition of $NaNO_3$ will alter ionic strength on the reaction system. Illustration of counter ion role on giving shielding effect to the interaction between positive and negative ions is presented at Figure 9 [11].

$NaNO_3$ is a kind of inert activity salt and can be used to make an increase of ionic strength of solution, which will slow the growth and nucleation rate at the same time based on the decrease of the activity of precursor ions. Addition of $NaNO_3$ will give shielding effect to positive Fe ions and decreasing the possibility to be reacted and precipitated by negative OH^- ions. When $NaNO_3$ added before precipitation or being mixed with Fe-salt at first stage, the shielding was already take place even before nucleation which result in amorphous nature of nanoparticles nuclei.

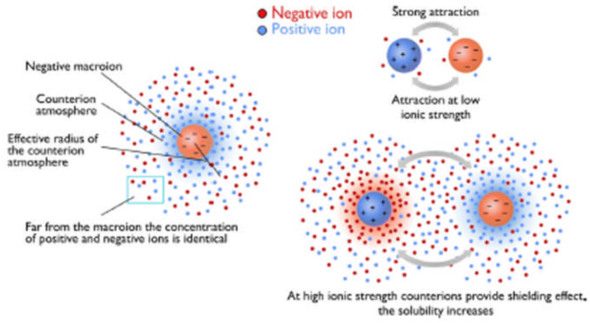


Figure 9. Schematic illustration of counter ion role on altering ionic strength between interacting macroion [11].

On the other hand, when $NaNO_3$ added after precipitation, $NaNO_3$ shielding around iron oxide nuclei will hindered diffusion of the ions afterward to the nuclei and inhibited further growth of nuclei. These analyses could explain the more stable particles size for 2nd series comparing to 3rd series. After all, $NaNO_3$ addition will slow down and inhibited the growth of nanoparticles to certain extent which depend on $NaNO_3$ molarity. Decreasing of M_s on $NaNO_3$ addition but rather insensitive to its molarity was also found as a result. Regarding all the parameters used within the synthesis and their characteristic, it can be proposed that modification with $NaNO_3$ of 6M molarity will give an optimum characteristic.

CONCLUSION

Size controlled magnetic nanoparticle (MNPs) of iron oxide have been prepared in the presence of $NaNO_3$ via co-precipitation method followed by peptizing with HNO_3. The magnetic nanoparticle properties including phase, crystallite size and magnetic properties were optimized by addition of HNO_3 and $NaNO_3$ in varied molarity and at different stage of process. As an end product, stable water-base colloids were formed, containing magnetic nanoparticle of Fe_3O_4/γ-Fe_2O_3 with nanoscale crystallite size. From data analyses result, it can be concluded that $NaNO_3$ addition will significantly affect crystallite formation due to its capability to increase ionic strength within the medium which slowed down the growth of magnetic nanoparticles and decreasing crystallite size. However magnetic hysteresis curve, measured using VSM, still displayed a typical superparamagnetic behaviour of magnetic nanoparticles with high enough magnetization value, M_s. At average, uniform magnetic nanoparticle with nanoparticles size of smaller than 10 nm, crystallite size and magnetic domain smaller than 8 nm and M_s value of 40 emu/gram is obtained for samples modified by $NaNO_3$ of 6M molarity and HNO_3 of 1M molarity.

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